European natural cements - their key technical properties under standardised conditions

HUGHES, David, WEBER, Johannes, STARINIERI, Vincenzo <http://orcid.org/0000-0002-7556-0702>, PINTER, Farkas, GOSSELIN, Christophe, FELDMAN, Steven and PESCE, Cecilia

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European natural cements - their key technical properties under standardised conditions

David Hughes[1], Johannes Weber[2], Vincenzo Starinieri[3], Farkas Pinter[4], Christophe Gosselin[5], Steven Feldman[6], Cecilia Pesce[2]

(1) University of Bradford, Bradford,UK d.c.hughes@bradford.ac.uk

(2) University of Applied Arts, Vienna, Austria johannes.weber@uni-ak.ac.at & cecilia.pesce@northumbria.ac.uk

(3) Sheffield Hallam University, Sheffield, UK v.starinieri@shu.ac.uk

(4) Federal Monuments Authority Austria, Vienna, Austria farkas.pinter@bda.gv.at

(5) Geotest SA, Le Mont sur Lausanne, Switzerland christ.gosselin@gmail.com

(6) National Institute of Standards and Technology, Gaithersburg, USA, steven.feldman@nist.gov

Abstract

The first comparative study on 7 commercially available Roman cements has been undertaken. In the absence of a European Standard, the testing procedures have followed a protocol proposed by the EU FP7 funded ROCARE project, which itself is based upon various ENs for cement and building limes. Evaluation has been made of mineralogy, particle size distribution, setting time, strength, water absorption, pore size distribution and mortar microstructure. Five of the cements required retardation and citric acid was used. The use of a pre-hydration technique was also investigated to extend the workable life of mortars to some 2 hours. The results confirm the view that the term Roman cement refers to a broad family of cements with a diverse range of properties which will need to be accounted for in future work to produce an all-encompassing Standard.

Introduction

Roman, or Natural, cement was a major material in the architecture of C19th Europe [1]. However, its use declined as Portland cement came to dominate each national market in turn. There has been a gradual increase in interest in these cements in recent years but the market is only supplied by relatively few producers. Calcined from marlstones at temperatures below sintering, Roman cements reveal compositions and properties which differ significantly from those of Portland cements. Whilst they are presumed to have a number of features in common, such as: rapid setting, delayed development of the final strength, high capillary porosity, and mostly good resistance against sulphate attack, an inherent feature is the variability in their performance dependant on the nature of the source marl, calcination conditions and any post-production processing.

Despite the small number of producers there is no single approach to specifying each cement and National Standards are not consistent [2, 3]. The aim of this paper is to assess key features of the cements available to the European market place using common methodologies based upon protocols developed during the EU FP7 funded ROCARE project 226898 [4]. This document modifies the procedures specified within EN 196-1 to adjust for the rapid set and the high water demand of typical Roman cements. The cements included in this programme are Prompt (Vicat, France), Folwark (Institute of Ceramics and Building Materials, Poland), Marfil (Cementos Collet, Spain), Cemento Rapido Figueres (Ciments Figueres, Spain), Tigre Rapido (Cemento Natural Tigre, Spain), Cemento Mallorquin (Sa Cimentara, Spain) and Natural Roman Cement, hereafter abbreviated to NRC (Roman Products, UK).

Methods

Mineralogy of each cement was determined by XRD powder analysis carried out with an X'Pert Pro PANAlytical diffractometer (Cu tube, λ=1.54 Å). The phase quantification by Rietveld analysis used an external standard (rutile) for the non-crystalline products. Particle size distribution was determined by laser diffraction using a Mastersizer 3000 from Malvern Panalytical using isopropanol as a dispersant; refractive index = 1.680. Three measurements per sample were taken. Examination was undertaken of final setting time of pastes produced at w/c = 0.65 and early age hydration pathway of pastes, produced at w/c = 0.6 (by XRD according to the same protocol as above).

Mortars were produced as per EN 196-1 using CEN sand, aggregate:cement ratio of 3:1 by weight and a w/c = 0.6. In order to produce mortars possessing a workable life suitable for sample production (~10 minutes) citric acid was incorporated into the mix water to provide suitable retardation (see Table 1). Cements NRC and Mallorquin did not require retardation.

Table 1. Modifications to mortars

Cement	Citric acid*	w/c
NRC	-	0.63
Mallorquin	-	0.68
Tigre Rapido	0.15%	0.62
Marfil	0.1%	0.67
Prompt	0.05%	0.60
Figueres	0.05%	0.70
Folwark	0.1%	0.60

* expressed as % by weight of the cement

Samples were produced for strength testing (EN 1015-11) at ages of 3 hours, 1, 7, 28, 91 & 270 days and water absorption coefficient (EN 15801) at ages of 28 and 91 days. These mortars were also observed using scanning electron microscopy (SEM). Vacuum impregnated polished thin sections prepared at mortar ages of 28 days were used to obtain detailed information on mortar fabrics and unhydrated residues, while the hydrated binders in respect to their morphological characteristics and pore structure were studied on fracture surfaces at ages of 28 and 91 days. The instrument used for SEM work was a FEG Quanta 250 SEM (FEI, U.S.A.) coupled with a Pegasus APEX energy-dispersive X-ray spectroscope (Ametek EDAX, U.S.A.) equipped with the Genesis SEM Quant software (SEM-EDX). Images were taken at high vacuum, for which the sections were coated with carbon while the fracture surfaces were gold sputtered. The acceleration voltage was 20 kV, using the backscattered electron mode (BSE) in all of the applications. In addition, the pore size distribution was determined by mercury intrusion porosimetry at an age of 91 days. The tests were carried out by means of a Pascal 140/240 mercury intrusion porosimeter from Thermofisher. The test specimens consisted of mortar fragments measuring approximately 5x5x10 mm collected from the core of each mortar beam. The samples were dried in a fan-assisted oven at 60 °C until constant weight prior to testing. The mercury contact angle was taken to be 140°.

During the production of these mortars the expected variation in workability – hence, water demand – was observed. Additional mortars were produced to a constant flow (EN 1015-3) of 17 ± 0.5 cm and tested for strength at ages of 7 and 91 days (the w/c ratio required to produce this flow is also shown in Table 1 and illustrates the varying water demand of the mortars). In order to produce these mortars a common citric acid content of 0.5 % was used where necessary, this being to allow the measurement of the flow unimpeded by any loss of workability due to rapid setting.

An alternative retardation approach has been previously reported [5] in which the cement is pre-hydrated by producing a damp sand and cement mixture and stored for specified time prior to final mortar production. The term De-Activated Roman Cement (DARC) has been adopted. Values of de-activation water of 10 % and 15 % (by weight of the dry cement) were used to prepare the “damp” mixtures which were then stored for 30 minutes. The mixing of the final mortar (w/c = 0.6) was the same as specified in EN 196-1 except that a prolonged high speed mixing time of 5 minutes after the “scraping of the bowl” phase was adopted. Workable Life was assessed according to EN 1015-9 with a target time of approximately 2 hours suitable for working with renders.

Data on anhydrous cements

Mineralogy

The composition of each cement is shown in Table 2 and three features are immediately apparent. By XRD each cement comprises both crystalline and amorphous phases; the latter of unknown composition but believed to be mainly calcium aluminates [4] and calcium-alumino-silicates [6].

Table 2.Composition of cements (% by weight)

Phase	NRC	Mallorquin	Tigre	Marfil	Prompt	Figueres	Folwark
β-C_2S	23	27	22	22	16	23	26
α'_H-C_2S	6	6	7	8	5	4	10
C_4AF	4	3	3	4	6	5	6
Lime	--	--	1	--	--	--	--
Periclase	4	1	3	1	3	1	1
Anhydrite	1	1	tr	2	1	1	--
Portlandite	5	2	6	3	5	8	5
Quartz	3	5	3	3	2	4	3
Calcite	20	19	17	18	19	15	11
Spurrite	8	6	11	9	13	10	10
Tilleyite	3	4	2	3	4	4	4
Gehlenite	4	7	5	11	7	7	8
Ye'elimite	--	--	--	1	2	2	--
Muscovite	2	--	2	--	--	1	--
Amorphous	20	20	19	16	18	17	17

Di-calcium silicate is the dominant phase, being present in four variants. Belite (C_2S) is observed in two polymorphs i.e. low temperature α'-C_2S and higher temperature β-C_2S. It has been previously confirmed that these phases co-exist with the proportion of α'-C_2S decreasing as the calcination temperature increases [7]. For the current cements the ratio of α'-C_2S to β-C_2S lies within the range 0.17 to 0.37; in contrast the ratio for "optimum" cements produced in a laboratory kiln, where the temperature gradients were kept to a minimum, is in excess of unity [7]. Carbonation of C_2S during calcination is evidenced by the production of both spurrite - $Ca_5(SiO_4)_2(CO_3)$ - and tilleyite - $Ca_5Si_2O_7(CO_3)_2$. The ratio of carbonated to un-carbonated C_2S generally lies in the range 0.3 – 0.5 with the exception of *Prompt* which registers 0.8. Previous data [6] shows a value similar to the other cements which suggests that the batch of *Prompt* from which the current sample was obtained may have undergone more carbonation within the kiln than usual.

Additionally, all cements show evidence of incomplete calcination as evidenced by residual quartz and surprisingly high amounts of calcite from low temperature areas of the kilns (Fig. 1a). The quartz is commonly observed as unreacted cores surrounded by calcium silicates (Fig. 1b). Evidence of high temperature phases such as ye'elimite ($Ca_4Al_6(SO_4)O_{12}$) and substantial quantities of gehlenite ($Ca_2Al_2SiO_7$) and belite clusters associated with melt formation (Fig. 1c) completes the picture of heterogeneous calcination conditions within many kilns. Free lime (CaO) is notable by its absence having been rapidly converted to portlandite ($Ca(OH)_2$).

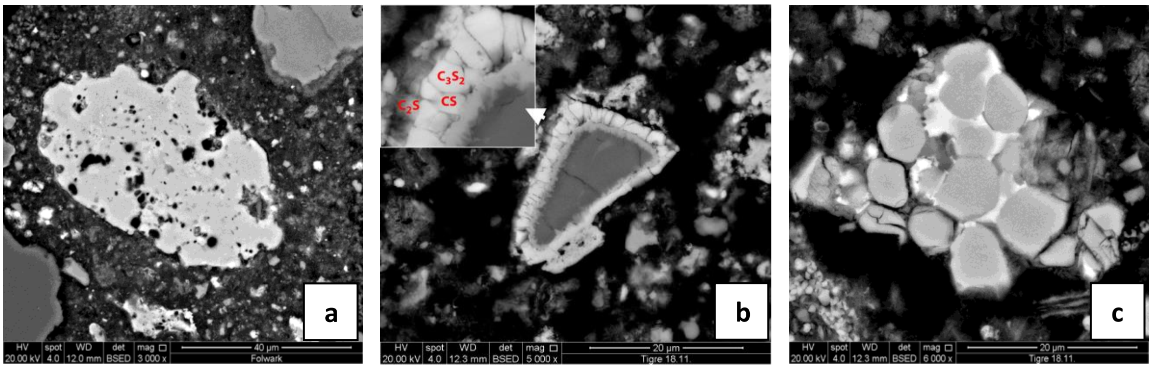


Figure 1. Characteristic constituents of natural cements, here observed as unhydrated residues in 28 days mortars; (a) calcite from the raw feed with thermally induced alterations as part of the underburned portion, (b) quartz with reaction rim containing increasing amounts of calcium towards the margin where crystals of CS, C_3S_2 and C_2S can be identified by EDX, see detail, (c) belite clusters with interstitial phase indicating initial melt formation as part of the overburned portion of the cement

Granulometry

The particle size data is shown in Figure 2. All cements have a similar maximum particle size although there are differences in the size distribution as shown by both D_{50} and surface area measurements. *Folwark* is clearly the finest cement and it is known that in the grinding process all oversize particles are re-ground until no residue remains. *Tigre* and *Marfil* only differ in the coarser regions whilst the remaining cements are similar except with differences in the coarser region, especially *Figueres*.

A comparison of the w/c ratios necessary to obtain mortars of common flow (Table 1) with the physical parameters (Fig. 2) reveals that there is no relationship between the data sets. This is not surprising since it does not account for the hydration occurring in these highly reactive cements during the time taken to mix the mortars and conduct the consistency test. Such an investigation is beyond the scope of the current study.

Final setting

Table 3 reveals a wide range of final setting times with *Figueres*, *Marfil*, *Folwark* and *Tigre* showing the rapid setting which is a common feature of Roman cements. It is understood that NRC undergoes a period of air-slaking of the calcined marl fragments before they are ground. As such, this is a commercial version of the DARC process previously described and has historical precedent [8] and the extended setting time is a consequence. However, the mineralogical analysis (Table 2) does not show the presence of early hydrated phases such as monocarboaluminate which was observed in de-activated *Gartenau* cement investigated in a previous project [5]. This may be a reflection of the *Gartenau* cement having been ground prior to de-activation whilst the NRC was exposed in much coarser fragments. In addition, *Gartenau* cement was exposed to surface water on the wet sand whereas NRC would have been exposed to atmospheric humidity.

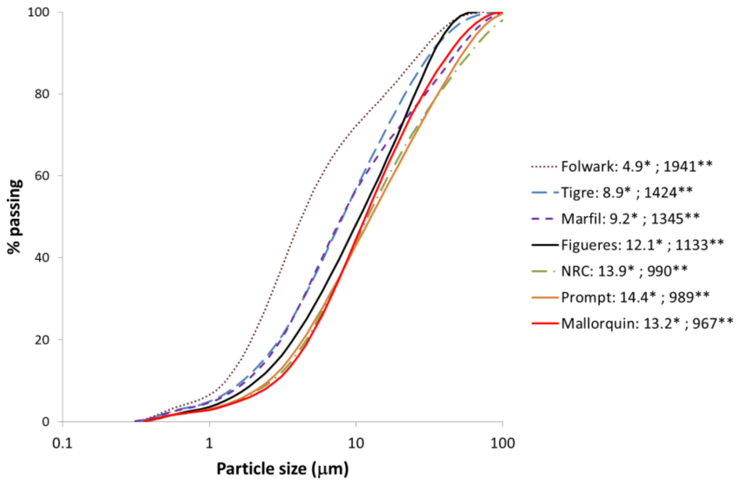


Figure 2. Particle size distribution * D_{50} (mm); ** Specific surface area (m^2/kg)

In contrast to the extended setting time measured for *Mallorquin* the manufacturer quotes a value of 19 minutes [9]; the reason for the difference is unexplained and is currently being investigated. Similarly, the setting time of *Prompt* is greater than we have previously measured.

Table 3. Final setting of pastes with no retarder (w/c = 0.65)

Sample	Setting time
Mallorquin	133 min
NRC	90 min
Prompt	30 min 30sec
Figueres	5 min 30 sec
Marfil	4 min 15 sec
Folwark	3 min 15 sec
Tigre	2 min 45 sec

Data on hydrated cements

Mineralogy

The compositions of pastes hydrated for 1 day are shown in Table 4. XRD shows the early age reactions to be dominated by alumina bearing phases with or without the inclusion of sulphate; note that all anhydrite has been consumed within 24 hours. As previously observed [6] *Prompt* yields a high content of ettringite with the raw cement having a high SO_3 content. In contrast, *Folwark*, with a low SO_3 content [10], produces no ettringite, but rather, the highest AFm content.

Any hydration of the belite phases is not readily shown by XRD since reaction is likely to be limited and any hydrates included within the amorphous phase, itself a contributor of alumina to the earlier reactions. Thus, any reaction can only be inferred from small decreases in belite content which may itself be masked by dilution of the cement content by the incorporation of hydrate water. Such early hydration has been previously reported by Hong and Young [11] and related to crystal size rather than to a particular polymorph. They showed that α'_L-C_2S with a surface area of some 40 m^2/g was fully hydrated within 7 days. In a previous study [4] 2-day old pastes of different cements were observed in the SEM. Despite the limitations of the small spatial resolution of the EDX point analysing system preventing quantifiable analysis of single phases, evidence of C-A-S-H phases was apparent.

Table 4.Composition of pastes hydrated for 1 day (% by weight)

Phase	NRC	Mallorquin	Tigre	Marfil	Prompt	Figueres	Folwark
β-C_2S	20	24	19	19	16	20	25
α'_H-C_2S	3	5	4	5	4	3	5
C_4AF	3	2	3	2	3	3	2
Periclase	3	1	2	1	2	1	1
Portlandite	3	1	3	--	1	4	2
Quartz	3	5	3	3	2	3	3
Calcite	20	18	19	18	17	14	9
Spurrite	6	5	7	5	9	7	6
Tilleyite	3	5	1	1	2	3	4
Gehlenite	5	9	4	12	6	10	10
Muscovite	2	1	2	1	--	--	--
Ettringite	7	6	4	7	11	7	--
Monocarbonate	5	1	8	2	3	6	10
Hemicarbonate	2	1	4	--	6	3	5
Monosulfate	--	--	--	1	--	--	--
Solid solution AFm (8.47Å)	--	--	--	5	--	--	--
Wollastonite	--	4	--	--	--	--	4
Amorphous	17	14	19	20	20	16	15

Properties of mortars

Microscopy

While polarising microscopy on thin sections, an important tool to characterise mortars and identify natural cement binders, is not presented in this contribution (examples are given e.g. by Weber et al. [12]), SEM studies on fractures of 28 and 91 days mortars illustrate the microstructural evolution of the hydrated matrix in terms of the shape and size of hydrates and the continuous though not complete closing of early age capillary pores (Figure 3 shows the extremes of WAC data; see Table 6).

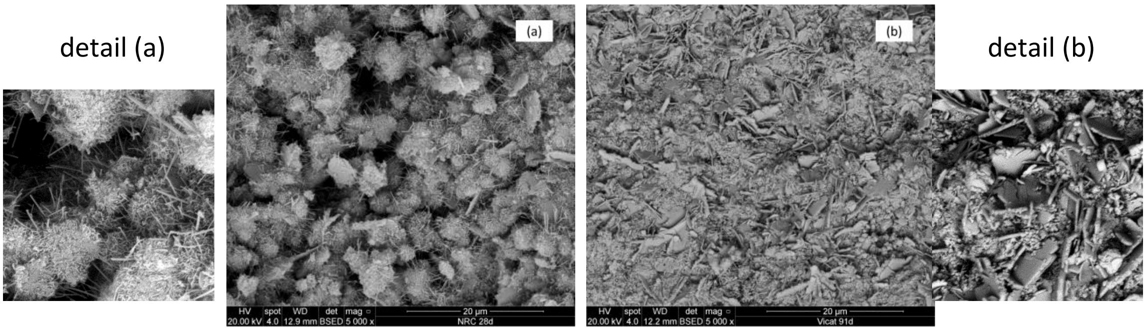


Figure 3. SEM micrographs of (a) *NRC* at 28 days and (b) *Prompt* at 91 days

Pore size distribution

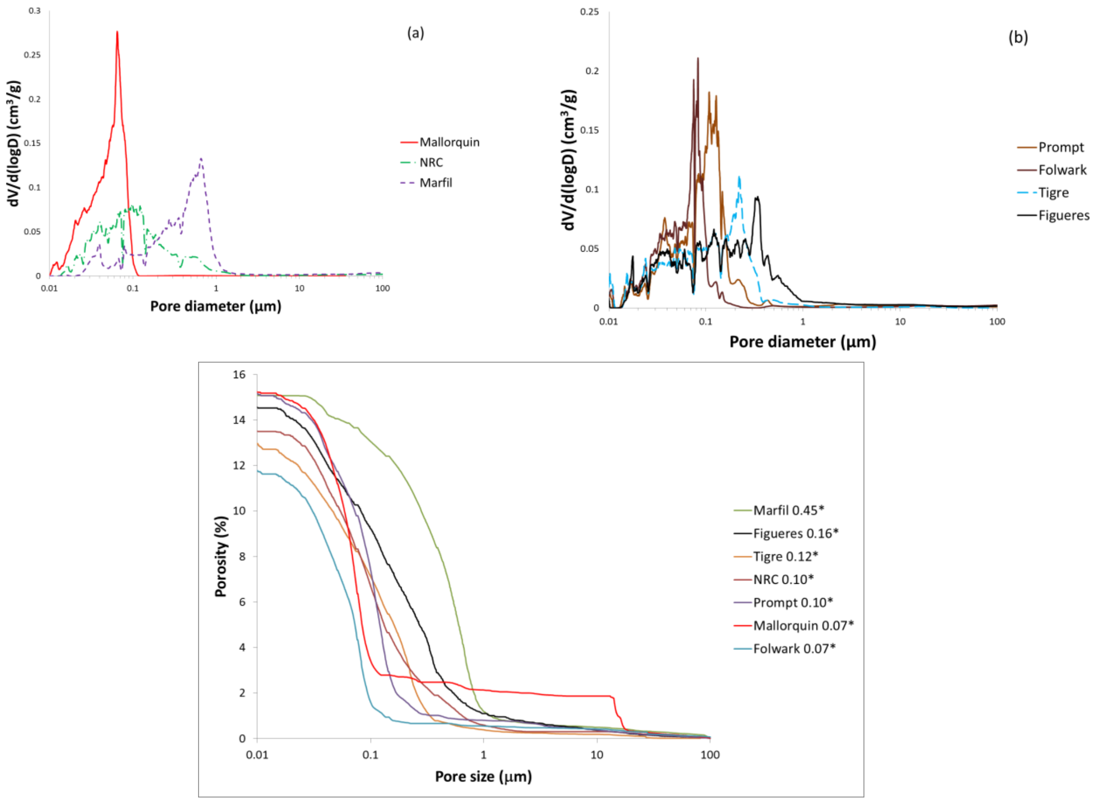
Figure 4 shows the pore size distributions of all mortars at an age of 91 days. The uni-modal distribution typical of mature Roman cements [e.g. 13] is exhibited. Of all cements *Prompt* and *Mallorquin* show the most restricted distribution in the 0.1 μm range; in contrast, *Marfil* exhibits the widest distribution.

Strength

Compressive strength development of mortars made at a fixed w/c = 0.6 is shown in Figure 5 for ages between 3 hours and 270 days; *Mallorquin* was too weak to demould for testing at 3 hours. The commonly observed profile of the initial very early age strength being maintained through a "dormant" period until a phase of rapid strength development is apparent for all cements; the onset of the latter phase is cement dependent and may not occur until an age of at least 28 days. All cements, with the possible exception of *Folwark*, suggest the potential for significant strength increase after 270 days, the last test age in this programme. The differing profiles illustrate the challenge faced by trying to select a single age at which to specify the strength of Roman cements for classification purposes. This may be illustrated by considering *Folwark* and *Marfil* cements; whilst *Marfil* shows the lowest strength of all cements at 28 days and *Folwark* the highest, there is no statistical difference between the two cements at 270 days. As a consequence of both long setting times and low strength, *Mallorquin* and NRC would not generally be considered ideal for the rapid production of cast elements.

In light of the potential hydration of the C_2S phases observed at 1 day it would have been expected that strength would have increased at early ages rather than be static.

However, it is possible that changes to the chemistry of the pore solution reduce the solubility of the C_2S phases to the extent that its hydration is temporarily suppressed. The concentrations of lime and Al in solution may have this effect although their impact has only been previously studied in relation to the hydration of Portland cements [14].



* median pore size (μm)

Figure 4. Pore size distributions of mortars; (a) & (b) - derivative, (c) - cumulative

The porosity of the mortars at 91 days generally lies in the range 12 – 19% by volume (Fig. 4) whilst the commensurate strength is in the range 7 - 21 MPa. There is no correlation between strength and porosity, whether total porosity or by excluding the finest pores. During an earlier EU funded project (ROCEM EVK4-CT-2002-00084) many cements were calcined under controlled kiln conditions in the laboratory and the development of pore structure of pastes of 3 of them over a period of 26 weeks have been previously reported [14]. Re-analysis of this data, taking an arbitrary measure of coarse porosity being that in pores >0.03 μm, and correlating with their strengths shows an interesting behaviour (Fig. 6). At high values of porosity (>0.3 cm^3/g) there is a good relationship between strength and porosity; however, at lower values of porosity, as found in more mature pastes, much more scatter is observed. Whilst the porosity of the current mortars (Fig. 7) is less than that of the pastes due to the presence of the sand, the porosity of their paste fraction is likely to be in the similar range of low porosity and high scatter, which may offer an explanation for the lack of correlation obtained in the current study.

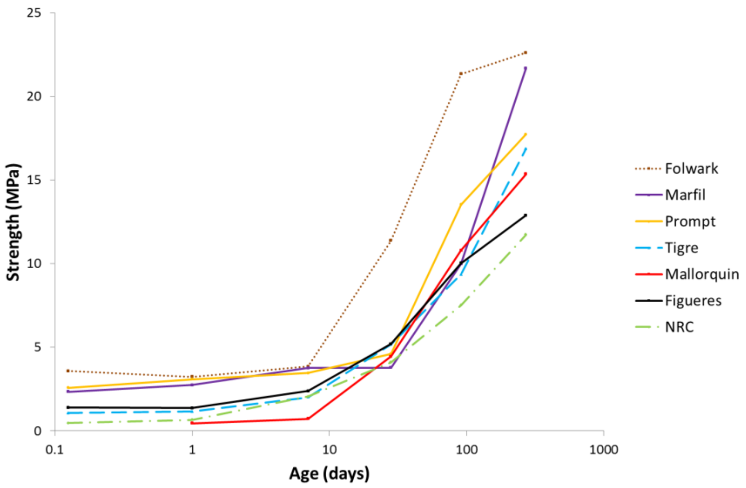


Figure 5. Compressive strength development of mortars produced at w/c = 0.6.

It is often said that production of mortars to a constant workability yields more practical information than the standard mortars produced at a constant w/c. Thus, a small programme was undertaken as previously described (see Table 1).

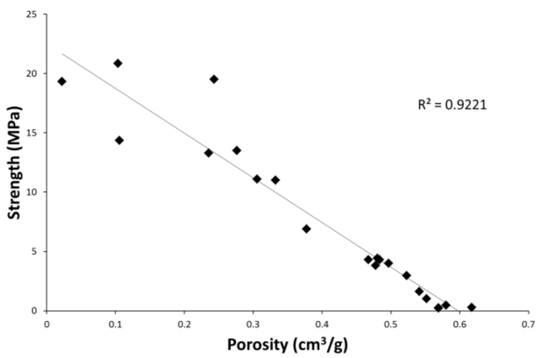


Figure 6. Strength – porosity >0.03 µm relationship of ROCEM pastes.

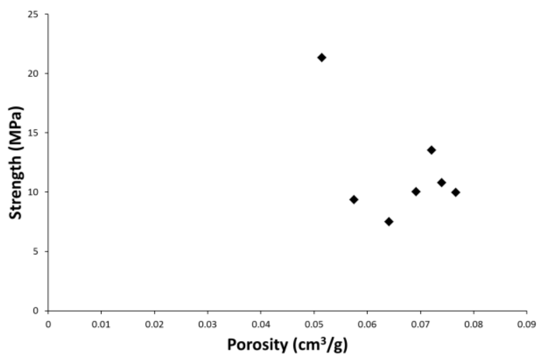


Figure 7. Strength – porosity >0.03 µm relationships of ROCEM mortars.

Figure 8 shows the comparison of strengths at ages of 7 and 91 days; the values in parentheses are the w/c ratios for the mortars of constant workability which were produced with a citric acid content of 0.5 % with the exception of NRC and *Mallorquin*. The effect of the differences in concentration of citric acid between the two series is apparent by considering *Folwark* and *Prompt* cements which have the same w/c in both series. At an age of 7 days the additional citric acid has had no significant effect on the strength of *Promp*t, whilst it has reduced the strength of *Folwark*; however, at 91 days the increased retarder has reduced the strength of *Promp*t but increased the strength of *Folwark*. Such behaviour has been previously observed during the ROCARE project.

Neither *Mallorquin* nor NRC required the retarder but did require additional water to deliver the required flow. However, the strengths of these mortars are higher at 91 days than the original set at w/c = 0.6. It may be that the additional workability permitted better compaction.

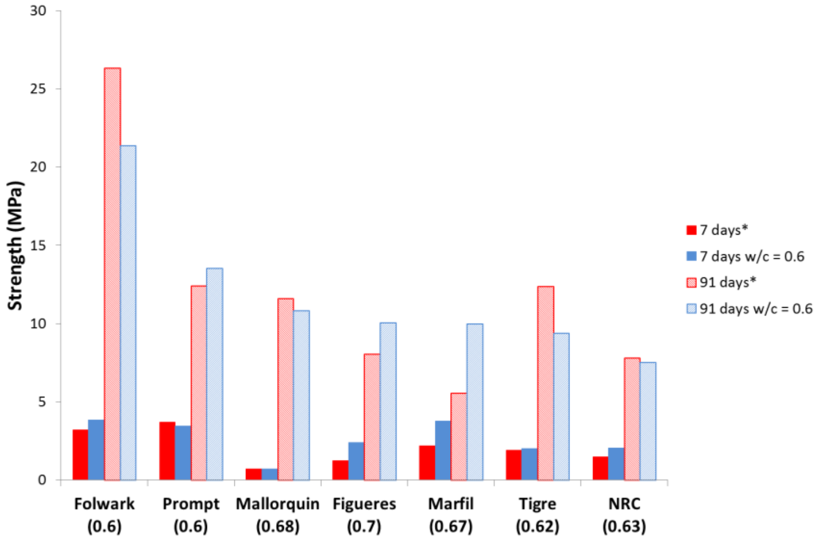


Figure 8. Comparison of strength for mortars produced at constant w/c and constant workability*.

Of the remaining cements both *Figueres* and *Marfil* exhibited expected behaviour with the highest strengths at each age aligning with the lower w/c ratio. However, *Tigre* performed similarly to *Folwark* in that the strength at 91 days was higher for the slightly higher w/c again suggesting a beneficial influence of the additional retarder.

Given the observed potential for citric acid to influence strength in a variety of ways it is not possible to reliably classify each cement when mortars are produced to a constant workability when retarded by 0.5 % citric acid and further study is required.

Water Absorption Coefficient

The WAC data at ages of 28 and 91 days is shown in Table 6 and it can be seen that, with the exception of *Folwark*, the WAC has reduced with age. A feature of enhanced curing of *Folwark* is the appearance of microcracks which are visible in thin sections (not included within this paper). These may account for the small increase in WAC between 28 and 91 days but not sufficiently extensive to substantially impact on strength development. It is generally the case that the two slow setting cements, NRC and *Mallorquin*, possess the highest values of WAC. No correlation between WAC and pore structure as determined by MIP has been established; probably as a result of the well-known limitations of the MIP technique. However, a qualitative interpretation of the micrographs in Fig. 3 generally shows a densification of the microstructure as the WAC reduces (Table 6).

Table 6. Results of Water Absorption Coefficient (kg/m^2/h$^{0.5}$).

WAC (kg/m^2/h$^{0.5}$)	**NRC**	**Mallorquin**	**Tigre**	**Marfil**	**Figueres**	**Prompt**	**Folwark**
28 days	4.57	3.57	4.04	2.81	3.40	2.50	1.31
91 days	3.20	2.91	2.29	1.97	1.87	1.28	1.41

Figure 9 shows the poor correlation between WAC and strength, further emphasising the limitations of relying on the specification of strength, despite its simplicity, to fully describe the in-situ performance of cements.

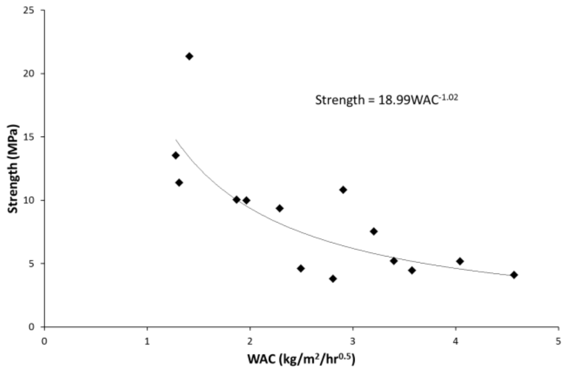


Figure 9. Correlation between strength and water absorption coefficient at 28 and 91 days.

De-activation as a method of retardation

It has been previously reported that this process might not be universally appropriate to all Roman cements [5]; thus, the opportunity was taken to assess the technique for the 5 rapid setting cements. The intention was not to determine optimum processing conditions such that more detailed study may be required before embarking upon its exploitation. The factors which have been used to control workable life were (1) the de-activation water (%), (2) the storage time before the final mortar was produced (mins) and (3) remixing the mortar upon the first reduction in workability. Thus, a mortar might typically be expressed as 10 %/30 mins.

As has previously been observed *Prompt* does not respond to this treatment, possibly as a result of the high ettringite production in early hydration. Indeed, a 10 %/30 mins mortar actually lost workability more rapidly than the control whilst having the same workable life.

The workable life is determined as the time when the penetration load reaches 1500 g; at this stage the mortars were re-mixed. As has been previously observed [5] after re-mixing whilst the workability is restored the rate of workability loss is reduced. In both cases the final workable life has exceeded the target life of 2 hours. It is apparent that, despite requiring more de-activation water, *Figueres* mortar loses workability at a faster rate than does *Tigre* (Fig 10). *Marfil* shows a similar performance to *Figueres* in the first phase but after re-mixing loses workability at a slightly faster rate. Thus, these

3 cements have the potential to be suitably retarded by the DARC process without the use of chemical retarders.

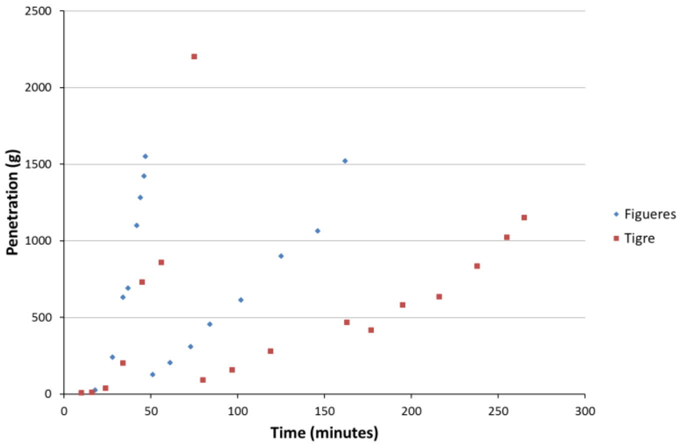


Figure 10. Raw data from Workable Life test for *Figueres* (15 %/30 min) and *Tigre* (10 %/30 min).

Samples for strength testing were made at the outset of the Workable Life test (A) and immediately after re-mixing (B). Strengths at 7 and 42 days are shown in Table 7 together with 7 day strength and an estimate of 42 day strength from the earlier reported programme. All strength differences between A and B occurrences are statistically significant. Thus, it can be seen that at 7 days 2 of the cements show a small decrease in strength following re-mixing whilst only a single cement shows the same at 42 days. Using *Gartenau* cement it has been previously shown that re-mixing has little or no impact on strength at ages between 7 and 91 days. Table 7 also shows that in comparison with the 3:1 mortars at w/c = 0.6 their DARC companions are weaker at both ages. In part this is a consequence of the DARC process; whilst also having been produced at the same w/c ratio they had previously been de-activated with water which if accounted for would raise the w/c ratio to at least 0.7. Even at an age of 42 days the strength of DARC *Marfil* is much below that of the "control"; this may be a reflection of the longer "dormant" period shown by this cement (see Fig 5).

A DARC *Folwark* mortar (15 %/30 min) was produced. Upon mixing the mortar had a "crumbly" texture; however, immediately upon mixing after the "scraping" phase it turned into a very "creamy" consistency. It recorded a workable life of some 21 hours. An additional mix was made with the inclusion of 0.2 % citric acid with the intention of overcoming the crumbly texture phase. Not only did this fail but the workable life was in excess of 2 days. The strength of the first mortar was 1.3 and 10.3 MPa at 7 and 42 days respectively in comparison with 3.9 and 13.6 MPa for the "control" samples. Much further work should be undertaken before any recommendation can be made on the applicability of DARC with *Folwark*; a training programme for prospective renderers is considered essential.

Table 7.Strengths of DARC mortars at ages of 7 and 42 days.

	7d (A)	7d (B)	7d	42d (A)	42d (B)	42d est
Tigre	1.36	0.89	2.01	5.10	4.56	6.10
Marfil	0.36	0.40	3.75	0.67	0.93	5.16
Figueres	1.63	1.42	2.38	4.61	4.96	6.27

Conclusions

This study has shown that:

1. All cements possess a mineralogical composition including both low and high temperature compounds indicating a range of calcination conditions within each kiln. With the exception of *Folwark*, the particle size distributions are broadly similar. There is no correlation with variations in mortar workability and early age reactions should be accounted for.

2. Two cements are slow setting, one is moderate and four set rapidly. The early age hydration is influenced by the sulphate content in each cement, producing both ettringite and AFm phases.

3. The pore size distribution at 91 days is typical of mature Roman cements, being uni-modal but with the median pore size varying by nearly one order of magnitude. Porosity is in the range 12 – 19 %.

4. Strength development follows a commonly observed path of the 3 hour strength being maintained for up to 28 days before a period of rapid strength gain occurs. Most of the cements suggest the potential for further strength gain at ages beyond 270 days.

5. The use of citric acid has a complex and inconsistent influence on strength development.

6. The WAC reduces between 28 and 91 days and shows poor correlation with strength. There is also no simple correlation with pore size distribution as measured by MIP; the same holds for strength and porosity.

7. Whilst *Tigre*, *Figueres* and *Marfil* respond beneficially to pre-hydration in order to extend workable life the latter is still weak at an age of 42 days.

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